Short communication

Electroactive separator for high voltage graphite/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ lithium ion batteries

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HIGHLIGHTS

▶ Spinel type LiNi$_{0.5}$Mn$_{1.5}$O$_4$ was successfully cycled *vs.* graphite in pouch cells for more than 700 cycles.
▶ Standard electrolyte was used in combination with a special electroactive separator (which contained lithium titanate).
▶ Oxidative electrolyte decomposition products were mainly responsible for cell degradation.
▶ Electroactive separator traps electrolyte decomposition products and prolongs lifetime of electrochemical cell.

ARTICLE INFO

ABSTRACT

The interaction of charged LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes in contact with standard electrolyte solvents as *e.g.* ethylene carbonate and ethyl methyl carbonate is investigated. Due to the high electrochemical potential of the charged LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode electrolyte decomposition occurs, which results in the formation of gases and other compounds. The corresponding decomposition products are successfully detected and analyzed by means of gas chromatography. We propose that decomposition products react on the surface of the graphite anode, which leads to strong capacity fading. Therefore, an electrochemically active separator containing Li$_{4+x}$Ti$_5$O$_{12}$ is used in graphite/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cells in order to scavenge and neutralize these decomposition products as well as soluble transition metal ions. This separator most probably prevents the migration of decomposition products to the anode and their subsequent reaction on the anode surface. Pouch cells with graphite anode, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode, standard electrolyte and the Li$_{4+x}$Ti$_5$O$_{12}$ based separator are cycled successfully for hundreds of cycles without any significant capacity fading. In contrast, similar cells equipped with a conventional separator show strong degradation.

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1. Introduction

LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (HV-spinel) is a promising cathode material for high energy lithium ion batteries [1–3]. When HV-spinel cathodes are combined with graphite anodes, average cell voltages of ~4.6 V are achieved. This enables an increase in energy density when compared to standard cathode materials.

Cycling behavior in half cells is good, but in full cells capacity is rapidly deteriorating [4]. Unfortunately, the high electrochemical potential of the cathode results in continuous electrolyte decomposition [5,6]. We have investigated the electrolyte decomposition and identified compounds which were generated at the interface of a charged HV-spinel cathode. The results are presented in this paper.

The decomposition of electrolyte and Mn^{2+} release from the cathode are believed to be the main reasons for the rapid capacity fading of graphite/HV-spinel cells during long term cycling. Up to now, this problem was addressed *e.g.* by doping [7,8] or coating of the cathode particles with *e.g.* ZnO [9], ZrO$_2$ [10], or even precious metals, *e.g.* gold [11]. However, such modifications to the active material can affect lithium diffusivity as well as cell resistance, and they result in additional costly process steps, which are difficult to implement in industrial scale production of LiNi$_{0.5}$Mn$_{1.5}$O$_4$. In a different approach to improve cycling stability, we used a separator containing Li$_{4+x}$Ti$_5$O$_{12}$ in order to scavenge decomposition products and transition metal ions. This separator prevents the migration of corresponding species and impurities to the anode surface, where they would subsequently react. Modifying the separator has the advantage that the preparation process for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ particles does not have to be modified by additional costly steps required for doping or coating of the material.

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2. Experimental

2.1. Preparation of electroactive LTO-separator

A slurry of 90 wt.% $Li_4Ti_5O_{12}$ (LTO), 7 wt.% polymeric binder (polyvinylidenfluorid hexafluoropropylene copolymer (PVDF-HFP), KYNAR FLEX® PPA 2801), 3 wt.% carbon black (Super P-Li, Timcal) in N-ethyl-2-pyrrolidon (NEP) was prepared by stirring over night with a magnetic stirrer. This slurry was coated on a PET non-woven by doctor blading which was then dried in a vacuum furnace at 120 °C over night. A typical loading of 8.5 mg cm^{-2} LTO was achieved. Subsequently, this 'LTO-separator' was lithiated by immersing it over night in 10 ml of n-butyl-lithium (15 wt.% in n-hexane). This step was done in an argon filled glovebox. During lithiation the LTO-separator changed its color from gray to black. Pristine LTO is white, but due to the carbon black content of the coated layer, the appearance is gray, which easily allows determining the quality of the LTO layer on the white non-woven prior to lithiation. The carbon black furthermore ensures a good electronic conductivity within the LTO layer which was found to be essential for a proper functioning. After lithiation, the sheet was thoroughly washed in n-hexane (>99% purity, BASF) in order to remove the n-butyl-lithium, which would otherwise react with the carbonate components of the electrolyte. The n-hexane was removed by washing in ethyl methyl carbonate. Additional lithium loading was gravimetrically determined to be around 0.14 mg cm^{-2}. As the theoretical capacity of LTO is 175 mAh g^{-1}, resulting in a maximum lithium storage capability of ~0.34 mg cm^{-2} for a separator with LTO loading of 8.5 mg cm^{-2}, it can be assumed, that the LTO was only partially lithiated, despite the over night soaking in n-butyl-lithium and the final composition of the lithiated LTO in the separator was $Li_{4+x}Ti_5O_{12}$.

2.2. Preparation of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ cell

First, a slurry was prepared from 88 wt.% $LiNi_{0.5}Mn_{1.5}O_4$ (BASF), 3 wt.% carbon black (Super P-Li, Timcal), 3 wt.% graphite (Timrex® KS6, Timcal) and 6 wt.% PVDF-HFP (KYNAR FLEX® PPA 2801) with NEP as solvent. Notably, carbon black, graphite and binder were all battery grade materials. The composition is comparable to a commercial battery electrode. The cathode slurry was coated on aluminium foil (AW 1050A O/H111, rolled sheet, 99.5% Al, 11 cm width, 30 μm thickness) using a lab coater (Coatmaster 509 MC, Erichsen). The coating speed was 5 mm s^{-1}. The width of the coated layer was always 8 cm. The foil was cleaned with ethanol prior to the coating process. The anode slurry contained 94 wt.% graphite (Cpreme, ConocoPhillips) as active material and 6 wt.% polymeric binder (PVDF-HFP). It was coated on high purity battery grade copper foil. Within a few minutes after coating, the sheets were carefully transferred to a plain glass plate and inserted into a vacuum-drying furnace. The coated layer was dried at 120 °C under vacuum over night. Higher drying temperatures would affect the polymeric binder as well as the active material.

After drying, the electrode was calendered between two steel cylinders in a calendering unit (Sumet Messtechnik). Calendering was carried out at room temperature with a speed of 50 cm min^{-1} and a constant linear load of 12 N mm^{-1}.

From the electrodes and the electro-active LTO-separator, a pouch cell was assembled as demonstrated in Fig. 1. Lithiated LTO has a high electrical conductivity. Therefore, three layered separator sandwiches were prepared using a polyolefin separator sheet (Celgard 2340) on each side in order to avoid direct contact to the electrode surfaces.

Cathode pieces (ca. 5 cm × 5 cm) were punched out by using a precision steel die. Tab leads were joined by ultrasonic welding (UltraWeld 40IA Branson). Anodes were prepared with a size of
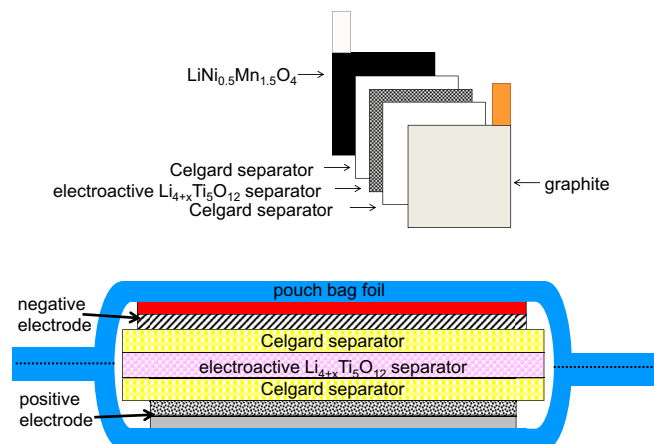

Fig. 1. Set-up of pouch cell comprising electroactive separator. Exploded view (top) and cross section.

5.6 cm × 5.6 cm, in order to ensure overlapping. On cathode side, aluminum tabs (Sumitomo) were employed. Anodes were joined with nickel tabs (Sumitomo). The size of the separator layer was always 6 cm × 6 cm in order to avoid short-circuits.

All cell components were transferred into an argon atmosphere glovebox (M. Braun). H_2O content was less than 1 ppm and oxygen content was less than 10 ppm. In order to reduce permeation, the box was equipped with 0.4 mm butyl gloves and kept under overpressure (~3 mbar). The electrolyte was always stored inside the glovebox, in order to avoid contamination with moisture or atmospheric gases. Electrodes (with tabs) were dried inside the glovebox at 5 mbar at 120 °C over night. Polymer separators were dried at 5 mbar and 60 °C over night.

After adding the electrolyte (1 M $LiPF_6$ in 1:1 mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), BASF), the cells were heat sealed and removed from the glovebox for electrochemical testing.

2.3. Electrochemical testing and post-mortem analysis

The cells were placed between two aluminum blocks. In order to level the pressure constantly on the whole area of the cell, PTFE-foam (Gore) was used and a defined stack pressure was applied. The tabs were then connected to a Maccor Series 4000 battery tester. Cycling was done in CC/CV mode. A constant current (CC) of 0.2 C was applied until a voltage of 4.8 V is reached. Then, the cell was charged at this constant voltage (CV) for 30 min, followed by discharging to 4.25 V. After two formation cycles at 0.2 C, the charge/discharge rate was increased to 1 C. After 50 cycles, three cycles were done with 0.2 C again, followed by another 50 cycles at 1 C and so on until the 1 C discharge capacity of the cells dropped below 80% of the initial discharge capacity.

2.4. Accelerated aging of EC/EMC at high cathode potential

In order to investigate possible reactions of the carbonates with the 5 V cathode, a graphite/$LiNi_{0.5}Mn_{1.5}O_4$ pouch cell was assembled using a binder free glass fiber separator (Whatman GF/A) instead of the LTO separator sandwich. The cell was charged in order to completely de-lithiate the cathode. The charging was stopped at a cell voltage of 4.8 V. Subsequently, the cell was disassembled in an argon filled glovebox. The fully de-lithiated cathode was removed and rinsed with dry EMC, in order to remove

residual $LiPF_6$. The electrode was then submerged in $\sim$2 ml of a 1:1 mixture of EC and EMC (without conductive salt $LiPF_6$) and stored at elevated temperature (45 °C) in a gastight bag of aluminum laminate foil, for 10 days. The carbonate mixture started to decompose and the resulting products were collected from the bag by means of an evacuated syringe afterward. The gaseous phase (head space) as well as the liquid phase were analyzed by means of GC/MS. he same process was done with an uncharged (lithiated) $LiNi_{0.5}Mn_{1.5}O_4$ electrode for comparison purposes.

3. Results and discussion

3.1. Accelerated aging of EC/EMC at high cathode potential

The liquid phase of the carbonate mixture which was stored in the presence of the charged $LiNi_{0.5}Mn_{1.5}O_4$ electrode had a slightly brownish color after the aging step whereas the liquid phase of the carbonate mixture was colorless when stored with the uncharged electrode. Table 1 summarizes the analytical result of the gaseous phase derived by gas chromatography (inert gases are not shown in Table 1).

Significant amounts of CO_2 and CO are detected when the EC/EMC mixture was stored with the charged $LiNi_{0.5}Mn_{1.5}O_4$, whereas in the case of the uncharged $LiMn_{1.5}Ni_{0.5}O_4$ almost no gas formation occurs. It is assumed that the CO_2 is most probably formed at the interphase of the electrolyte and charged electrode due to electrolyte oxidation. Clearly gas formation is larger when charged $LiNi_{0.5}Mn_{1.5}O_4$ cathode material was used.
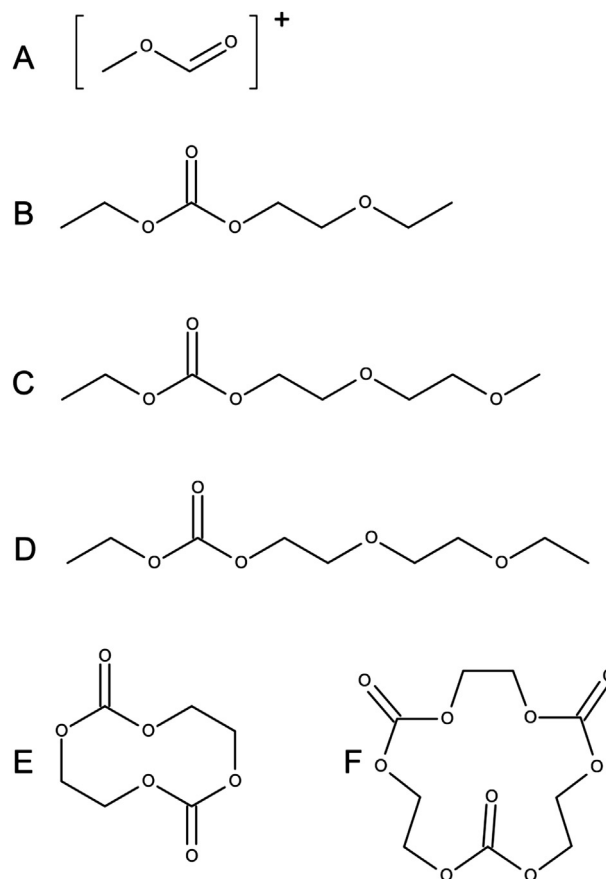
It should be noted that CO_2 can be reduced at the anode to yield oxalate and formate [12]. Oxalate may be reoxidized at the cathode back to CO_2 to provide a reversible self-discharge mechanism. Therefore, CO_2 may be responsible for high self-discharge rates and low coulombic charge/discharge efficiencies. CO_2 can also be reduced at the anode to CO, hydrocarbon and Li_2CO_3 in an irreversible discharge mechanism, which leads to strong capacity fading [13].

GC/MS analysis of the liquid phase of the bags revealed that EC/EMC reacts with the charged $LiNi_{0.5}Mn_{1.5}O_4$. It was observed that several additional compounds were generated in the case of the charged $LiNi_{0.5}Mn_{1.5}O_4$ electrode when compared to the uncharged electrode. This confirmed the instability of the electrolyte with the charged electrode material at high potential. Structures were attributed to these peaks by means of mass spectroscopy. Besides water, *tert*-butanol, acetone and *bis*(2-methoxyethyl)ether, also the compounds **A**–**F** shown in Fig. 2 were observed. These compounds are linear oligo(ethercarbonates) and cyclic carbonates which were most probably formed by the ring opening of EC and its subsequent transesterification with EMC [14].

It was estimated that the concentration of these compounds was in the order of a few tens up to a few hundreds of ppm. The generated protic compounds (water and *tert*-butanol) do irreversibly react with the graphite anode. This results in significant capacity fading. Also aprotic compounds (acetone and *bis*(2-methoxyethyl) ether) or the charged compound **A** may react unfavorably with the graphite anode and probably lead to solvent co-intercalation which irreversibly destroys the anode during prolonged cycling.
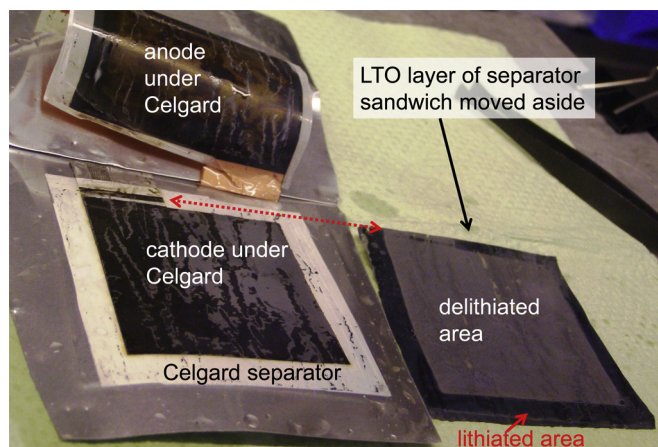

Fig. 2. Proposed structures of compounds formed in EC/EMC due to reaction with charged (de-lithiated) $LiNi_{0.5}Mn_{1.5}O_4$, besides water, tert.-butanol, acetone and bis(2-methoxyethyl)ether.

3.2. Electrochemical performance of graphite/$LiNi_{0.5}Mn_{1.5}O_4$ pouch cells

The discharge capacity of a graphite/HV-spinel cell containing the lithiated LTO-separator is shown in Fig. 3(A). The capacity of this cell at a 1 C discharge rate after 720 cycles is still around 80% of the initial capacity. In contrast, similar cells equipped with a conventional polyolefin separator and a non-lithiated LTO-separator,
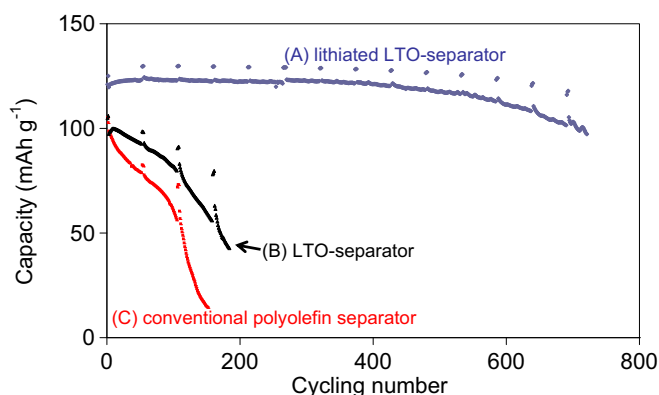
Fig. 3. Discharge capacity over cycle number of graphite/HV-spinel cells containing different separators: lithiated LTO separator (A), LTO separator (B), and conventional polyolefin separator (C). Current: 1 C with 3 cycles at 0.2 C every 50 cycles, respectively. Lower cut-off voltage: 4.25 V, upper cut-off voltage: 4.80 V.

Table 1
GC/MS analysis of gas phase after accelerated aging.

Gas	H_2	CO	CO_2
Charged cathode	<0.1%	1.25%	3.09%
Pristine cathode	<0.1%	<0.1%	0.48%

Fig. 4. Graphite/HV-spinel pouch cell containing lithiated LTO-separator, disassembled after 720 charge/discharge cycles.

respectively, show strong degradation as depicted in Fig. 3(B) and (C). Those cells show less than 80% capacity retention after ∼100 cycles or less.

We assume that the electrolyte oxidation products (*i.e.* protic species) are formed at the cathode and are subsequently migrating to the anode where they react on the surface which results in cell failure. Mn^{2+} leaching from spinel cathodes leads to poisoning of the graphite anodes [15]. In addition, CO_2 formed at the cathode when in discharged state will react to lithium carbonate on the anode. These processes lead to continuous irreversible loss of lithium at the graphite anode, which causes strong capacity fading.

Interestingly, these issues can be overcome by the use of the lithiated LTO-separator which prevents the migration of the decomposition products to the anode. $Li_{4+x}Ti_5O_{12}$ with a redox potential of 1.5 V *vs.* Li/Li^+ was found to be a very effective electroactive compound for this purpose. It is assumed that protic species as well as manganese ions are reduced directly at the surface of lithiated LTO. By means of elemental analysis using inductive coupled plasma (ICP) technique, the manganese content on the anode after cycling was found to be about 1 g cm^{-2} when the lithiated LTO separator was employed, whereas it was close to 3.5 μg cm^{-2} when the standard separator (A) was used, indicating that indeed the manganese migration is significantly reduced. It should be pointed out that electroactive compounds comprising a lower electrochemical potential than LTO (*e.g.* lithium powder) are not as effective as LTO for this purpose. This could be explained by the fact that then additional electrolyte decomposition occurs within the separator.

3.3. Post mortem investigation

After 720 cycles the cell containing the lithiated LTO-separator was disassembled in the glovebox under argon in the fully charged state. Fig. 4 shows a photograph of the opened cell. The LTO-layer of the separator sandwich is moved aside for better visibility. Both electrodes as well as all separator layers were still covered with electrolyte. Most interesting is the appearance of the lithiated separator: Prior to lithiation, the LTO-separator had a gray color but after lithiation it was completely black. After cycling, the separator is still black on the edges, but a large area in the center is

gray, indicating a non-lithiated state which exactly resembles the shape of the cathode. The reduced lithium content was confirmed by means of elemental analysis. The morphology of the LTO particles or the carbon black was found to remain unchanged by means of SEM investigation. CO_2 formed at the cathode in charged state might also react to lithium carbonate at the lithiated separator, thus removing the CO_2 from the system. However, the amount of lithium carbonate can be considered small, as by means of ICP a Li/Ti ratio of 0.13–0.14 was determined in the de-lithiated area of the separator. The Li/Ti ratio in $Li_4Ti_5O_{12}$ is 0.126, and residual conductive salt from the electrolyte cannot be excluded, which would affect the measurement.

4. Conclusions

It was shown that charged $LiNi_{0.5}Mn_{1.5}O_4$ cathodes gradually oxidize EC/EMC due to their high potential. Identified oxidation products were *e.g.* traces of CO_2, CO, water and several organic species. These oxidation products are believed to interact with graphite anode causing low charge/discharge efficiencies upon cycling and strong capacity fading. An electroactive separator containing lithiated LTO was used to scavenge decomposition products as well as Mn^{2+}. Pouch cells with graphite anode, $LiNi_{0.5}Mn_{1.5}O_4$ cathode, standard electrolyte and an electroactive $Li_{4+x}Ti_5O_{12}$ containing separator were prepared and cycled successfully for hundreds of cycles without any significant capacity fading. In contrast, similar cells equipped with a conventional separator show strong degradation. It is assumed that this type of separator prevents migration of decomposition products formed at the cathode upon cycling from migration to the anode where they would subsequently react on the surface and reduce the lifetime as well as the C-rate performance of the battery.

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